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MOLECULAR METALS: NEW ORGANOMETALLIC SYSTEMS.(U)

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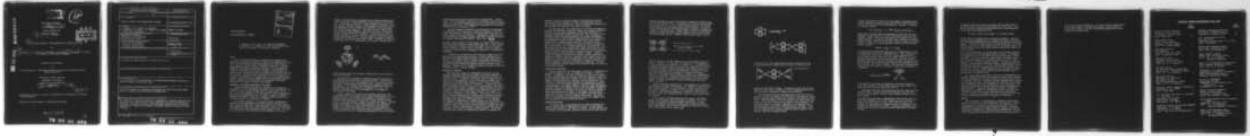
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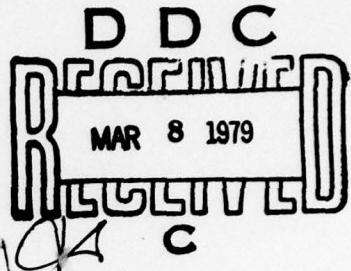
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## Molecular Metals: New Organometallic Systems

by

L. Alcacer, R.J.H. Clark, W.E. Hatfield, K. Klabunde, J.S. Miller, G.D. Stucky,  
G.A. Toombs, F. Wudi, and S. Yoshimura



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MOLECULAR METALS:

NEW ORGANOMETALLIC SYSTEMS

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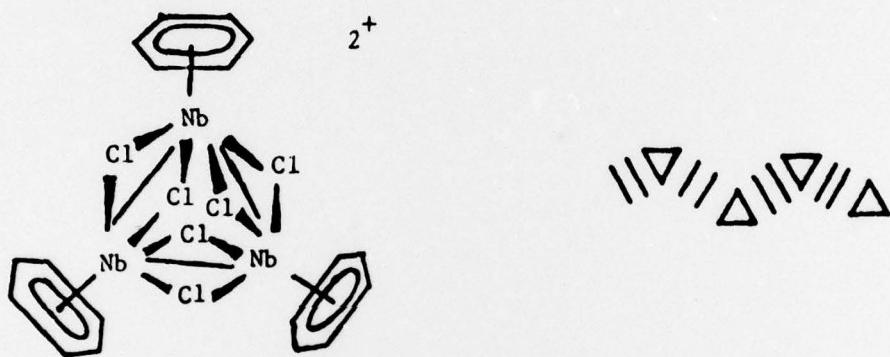
The two unique properties of organometallic systems which make them of particular interest for use in the synthesis of molecular metals and related solid state materials are their ability (1) to support a wide variety of oxidation states and to undergo reversible one-electron transfer reactions, and (2) to exist as chemically independent stable free radicals. The materials discussed in this report are limited to systems in which there are either direct metal-carbon bonds (excluding metal cyanide complexes) or in which a transition metal complex acts as either a donor or acceptor with respect to an organic group i.e. as a charge transfer complex. Main group metal systems such as sodium doped polyacetylene or graphite are excluded from the discussion as they are included in the reports of other study groups.

Assessment of Existing Knowledge of the Field

Transition metal organometallic chemistry is a relatively young field. By far the biggest expansion of our knowledge in this area has occurred during the past ten to fifteen years. It is fair to say that progress in the development of solid organometallic materials has lagged behind that of either organic or inorganic substances because of a lack of a systematic understanding of the synthetic aspects of organometallic chemistry.

The greatest application of transition metal organometallic complexes in the development of molecular metals has been their use as electron reservoirs, either as acceptor or as donor species. Some examples in this area include the early studies of ferricenium and cobalticenium TCNQ complexes by Melby *et al.* in 1962. An important variation on this approach was the synthesis in the early

1970's of "mixed valence" complexes such as  $(\text{bisfulvalenediiron})^{+}$ - $(\text{TCNQ})_2^-$  which has a compressed pellet conductivity of  $10-40 \text{ ohm}^{-1} \text{ cm}^{-1}$ . An example of the use of transition metal complexes to support unusual oxidation states is illustrated by the work of Miller and coworkers who have reported the isolation of the previously postulated  $[\text{Nb}_3\text{Cl}_6(\text{C}_6\text{Me}_6)_3]^{2+}$ . This was the first case in which the  $2^+$  ion had been isolated in the solid state as a consequence of the unusual properties of  $(\text{TCNQ})_2^-$ . The structure of the  $2^+$  monomer complex in the solid state is that of a bent chain configuration as indicated below, with the triangular cluster,  $[\text{Nb}_3\text{Cl}_6(\text{C}_6\text{Me}_6)_3]^{2+}$  alternating with a TCNQ<sup>-</sup> dimer. Although this material is not metallic, it is reminiscent of the organic charge-transfer



TCNQ complexes with donor-acceptor stacking which were discovered early in the 1960's.

The majority of attempts to synthesize molecular metals from organometallic materials have not been successful. Nevertheless, these studies have led to the preparation of particularly interesting weakly coupled systems which show unusual magnetic properties. For example, a 1:1 complex formed between decamethylferrocene and TCNQ has been found to behave as a metamagnet at 2.5 K. The material switches from an antiferromagnet to a ferromagnet at approximately 1500 Gauss.

Another example of a system which exhibits previously unreported properties is provided by the complex formed between TTF and  $\text{Cu}[\text{S}_2\text{C}_2(\text{CF}_3)_2]_2$ . This material was prepared by Interrante in an attempt to synthesize a transition metal charge transfer complex with TTF which was expected to behave as a molecular metal. Although he was unsuccessful in this attempt, subsequent low temperature magnetic and structural studies revealed that it was the first example of a system which exhibited a spin Peierls instability. Further experimental and theoretical work as described in the poster session has led to an enhanced understanding of the relationship

between weak interactions and structural instabilities. Similar types of solids have been reported to be reasonably good molecular metals, e.g. (perylene)<sub>2</sub>Pt[S<sub>2</sub>C<sub>2</sub>(CN)<sub>2</sub>]<sub>2</sub>, has a conductivity of approximately 200 ohm<sup>-1</sup> cm<sup>-1</sup>. The conductivity increases with decreasing temperature with a maximum at 120 K.

The above examples demonstrate the versatility of organometallic molecules in that they have a profound influence on the electronic and magnetic properties of the solids which they form with either organic donors or acceptors. Organometallic materials also have the ability to promote unusual solid state chemical processes. For example, [Pt(bipy)<sub>2</sub>]<sup>2+</sup>(TCNQ)<sub>2</sub><sup>2-</sup>, where bipy = 

has been recently shown by Keller *et al.* to undergo reversible carbon-carbon bond formation between TCNQ<sup>-</sup> molecules. As the temperature is raised two radical anions are formed, and as the temperature is lowered a covalent bond is reformed so that the material is readily converted from a diamagnetic insulator to a paramagnetic substance.

It should also be mentioned that numerous attempts have been made to attach organometallic groups to polymer backbones and to generate non-integral oxidation states in the resulting polymeric species. The conductivities of these investigated substances are in the semiconducting region primarily because there are relatively weak interactions between the adjacent metal atom sites in the polymers. Pittman has, for example, attached ferrocene in different oxidation states to organic polymers.

#### Scientific Potential

An attractive feature of organometallic materials is the extensive chemistry available for organic molecules augmented by chemistry associated with the changes in the oxidation states of the metal atoms. It should also be noted that one important driving force for the generation of new metal-carbon systems, particularly those involving metal clusters, is the recent increasing research activity and interest in catalysts. It seems very likely that this research will also lead to new organometallic materials with interesting transport properties. Recent advances in synthetic procedures, such as those applied in the syntheses of large metal clusters by Chini, and in metal-vapor deposition techniques, are particularly important in this respect. The majority of the synthetic work in organometallic transition metal chemistry has been directed towards the development and understanding of synthetic processes, both catalytic and stoichiometric. It is important that synthetic organometallic chemists be aware of the problems and needs in the area of solid state chemistry and physics so that a greater effort can be made to develop materials whose study would result in a better understanding of solid state phenomena and which would have new and useful physical characteristics. We strongly recommend that a group of predominantly synthetic organometallic

chemists along with a smaller number of physicists and physical chemists be called together to promote the development of this very important area of research. Such a program could appropriately be held under the auspices of the NATO ASI program.

For the most part, the limitations of utilizing organometallic materials are similar to those for organic and inorganic substances but there are the added advantages of increased flexibility in synthetic design and electronic properties. The following are two additional limitations which appear to be readily surmountable:  
(1) Dissociation of metal-carbon sigma bonds which are relatively thermodynamically stable leads to decomposition with formation of highly reactive organic radical species. The problem can be resolved by using fluorocarbons, delocalized organic groups which form stable anions, or  $\pi$  acceptor ligands such as CO and CNR  
(2) Electronic and structural properties of small organometallic molecular systems are not sufficiently well understood to enable one to design or predict the efficiency of electron transfer in macroscopic systems built up from the smaller molecular systems. Extensive studies of magnetic interactions in weakly coupled organometallic systems have laid an important foundation which together with future studies on strongly coupled interactions should enable preparative chemists working closely with physicists to prepare materials with specific magnetic, electrical, and optical properties. As noted below, additional research needs to be carried out which is directed towards this problem.

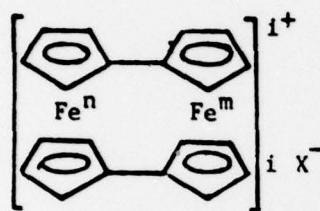
#### Technological Potential

We anticipate that the technological potential of organometallic materials is similar to that of organic and inorganic molecular metals. Consequently, the text of Yoshimura's lecture and reports of other study groups who have dealt with this important subject in detail should be consulted. However, we call attention to the following: An application that we expect to arise indirectly from the study of molecular metals derived from organometallic systems could make use of the unusual magnetic properties described above. Extended research on systems related to the very simple metamagnetic material  $[(C_5Me_5)_2Fe]TCNQ$  may lead to the development of magnetic switching devices. In addition, the study of electron transfer in these compounds should be useful in the design of electrochromic substances because of the variety of available oxidation states to which both the metal atoms and ligands have access. The recent report of metallocenes intercalated into TaSe<sub>2</sub> also suggest potential application in solid state electrodes.

#### Research Directions

A broader base of experimental data on weak and strong interactions between radical organometallic species is badly needed before real progress in this area can be made. We wish particularly to emphasize that systematic studies of the structural and chemical

features necessary to vary the electronic properties of semiconducting systems would be useful. An example is the series  $[(C_5H_xR_y)_2M]^{n+}$ , M = Fe, Co or Ni ( $x + y = 5$ ) R can be varied almost at will so that both electronic and structural effects can be studied. An example of one such system with interesting magnetic properties  $[(C_5Me_5)_2Fe]^-$  (TCNQ) has been given above. Another type of system of considerable interest includes the mixed-valence complexes such as those formed with bisfulvalene diiron. Mössbauer spectroscopy reveals only one



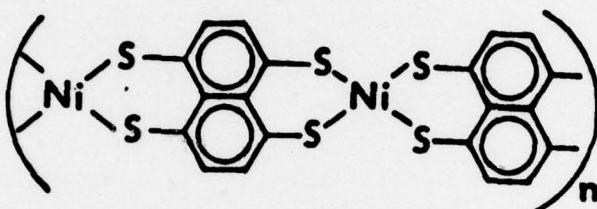
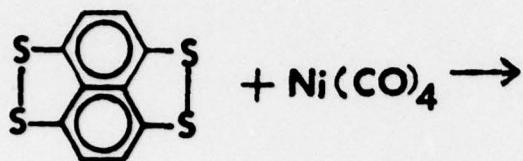
- la: n = m = 2, i = 0  
 lb: n = 2, m = 3; i = 1; X =  $BF_4^-$ ,  
     picrate,  $(TCNQ)_2$   
 lc: n = m = 3; i = 2, X =  $BF_4^-$

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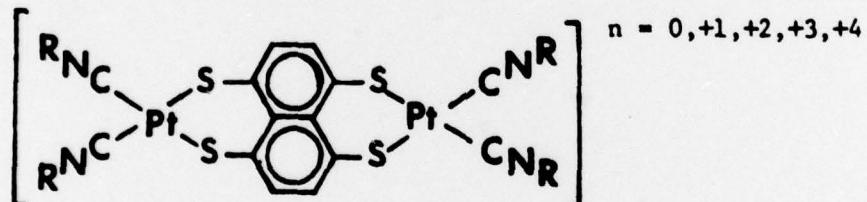
type of iron atom, and the conductivity of the compacted powder lb with X =  $(TCNQ)_2$  is of the order of  $20 \text{ ohm}^{-1} \text{cm}^{-1}$ . The mechanism of the conductivity is unknown, i.e. whether it is via TCNQ chains, or through the mixed valence iron units or a combination of the two. Studies of partially oxidized extended chains based on units such as the diiron complex above could certainly be expected to contribute significantly to our knowledge of cooperative transport behavior in low dimensional materials in general and organometallic species in particular. While we recognize that there are considerable difficulties in the synthesis and manipulation of these compounds, we expect that efforts focused on these problems would lead to solutions.

Another promising research area is the preparation of materials with direct metal-metal interactions. For example, an interesting and answerable question is the following: given large metal clusters such as  $M_x(CO)_y = A$ , where  $x \leq 20$ , are known, what would be the physical and chemical properties of polymeric species such as  $(-A-A-A-)$ , where the linkage consists of one or more covalent metal-metal bonds?

Also, since it was demonstrated by Teo, et al., and Engler, et al., that molecules which form organic conductors can be converted to ligand-metal bonded polymers (shown below), a large variety of polymers containing a combination of metal-metal and metal-ligand bonded solids could be prepared by reaction of  $M_x(CO)_y$  with a specifically chosen ligand; viz,



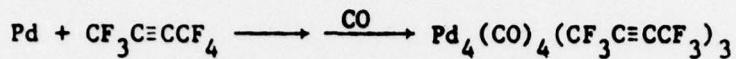
In the same vein, the compound below would be expected to form extended metal-metal bonded chains provided R is small and the



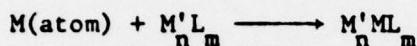
molecule is partially oxidized. In support of this, Teo and Wudl have shown that partial oxidation of the triphenylphosphine analog leads to stable intermediate oxidation-state species.

New techniques have been developed which allow the vapors of metals to be used as reagents for carrying out syntheses of organometallic species, many of which are related to the molecular metals field. These techniques allow the interaction of metal atoms such as Fe, Co, Ni, Pd, or Pt as well as those of other elements, with vapors of organic or inorganic compounds at low temperatures, or with solutions of nonvolatile compounds such as polymers. These new developments should serve to stimulate many new ideas in the area of organometallic molecular metals and metal dopants. Some specific ideas are enumerated below:

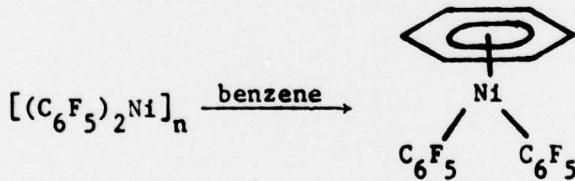
(1) The interactions of metal atoms with weakly complexing organic ligands followed by warming and partial M-M bond reformations has allowed the production of new organometallic clusters. An example is a new Pd<sub>4</sub> cluster:



Larger metal clusters where the nucleation is such that the metal aggregates become "particles" of 10-30 Å diameter have also been prepared. These clusters are stabilized by the presence of organic ligand fragments. In general the metal vapor technique holds great promise for the production of new metal clusters either by trapping growing clusters, or by inserting metal atoms into already formed smaller clusters:



(2) The metal atom method has been used for the generation of new "coordinatively unsaturated" organometallics. Thus, the insertion of a metal atom such as Pd or Ni into a carbon halogen bond to form an R-M-X species, where M is two ligands short of its normal tetracoordinate state, has been carried out. Molecules such as C<sub>6</sub>F<sub>5</sub>NiBr, C<sub>6</sub>F<sub>5</sub>PdBr, (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Ni, (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Co, CF<sub>3</sub>PdI, and C<sub>6</sub>F<sub>5</sub>PtBr have been prepared. These are polymeric materials (structures unknown) until an additional ligand is added. The unsaturated organometallic compounds are very reactive, and even a ligand such as benzene is coordinated:

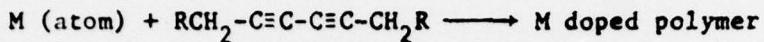


It is possible that these coordinatively unsaturated molecules would form metal-metal bonded chains under the proper redox conditions and with the correct choice of R and X.

Even TCNQ itself has been deposited with metal atoms yielding films of M-TCNQ. Further studies with TCNQ and other electron acceptors are desirable, with an initial emphasis needed on structural studies.

(3) Several reactive small organometallics have recently been prepared that decompose clearly upon warming of their solutions to deposit metal particles or films. Could these be used as new reagents for intercalation by magnetic metals of graphite or other important layered molecular metals? Successful experiments have already been carried out where Ni has been deposited in the pores of Al<sub>2</sub>O<sub>3</sub>.

(4) Recent metal atom studies have shown that Ni atoms serve to polymerize styrene with the incorporation of the Ni atom. This may be a method of doping polyacetylenes and/or diacetylenes and at the same time polymerizing them:



(M atoms serve as polymerization catalyst and dopant). Alternatively, polymer solutions could be treated with metal atoms using new rotating metal-atom reactors containing the partially dissolved polymer. In this way metal atoms may be incorporated in the polymer lattice, especially if the polymer swells in the solvent and if the solvent serves to carry the metal atom into the polymer (weak solvent-M complex).

(5) Vapor techniques for the preparation of active small molecules that polymerize to form the host are also possible. For example, the codeposition of C vapor and M vapor is now possible to form a  $C_x M_y$  film. It is not presently clear whether the product would be an intercalated graphite or a new metal-carbon species. Other small molecules could be studied similarly. All that is required is that a reactive small molecular fragment be generated and codeposited with M atoms on a cold wall. Some possible studies involving reactive molecular fragments would be CS + Ni, SN + Ni, CF<sub>2</sub> + Ni, SO + Fe, PN + Co. These studies are now experimentally possible and some interesting new conducting films probably could be generated on a synthetic scale.

The final example given here is the use of organometallic compounds as synthetic precursors for metallic films. This technique has been described in the literature and is the basis for at least one commercial process. Passing a volatile organometallic compound such as (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Cr over a surface heated to relatively mild temperature (~300°C) results in the formation of a thin metal film. The thickness of the film is readily controlled even to dimensions as small as 1000 Å. Schrauzer has applied a similar technique to organometallic compounds of niobium and tantalum to produce thin film alloys which have critical superconducting temperatures that are reported to be higher than those of alloys with the same chemical composition prepared by conventional techniques.

#### Summary

The application of organometallic compounds to solid-state physics and chemistry is only beginning to be examined in detail. The relatively few studies that have been done have been with organometallic molecules acting as electron donors or acceptors. Solid state materials with unique electric, magnetic and optical properties of significant potential have been produced. In particular organometallic molecules can be used to build systems which,

due to their relative simplicity, can bring a better understanding of the solid state. We believe that support should be given to this area of research and that the meeting proposed above should be held in the near future.

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